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Atmospheric Kinetics for Toxic Industrial Compounds (TICs)

Paper # 1066

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ABSTRACT

The modeling of the atmospheric dispersion of a chemical release has reached a high level of sophistication in the description of the physical distribution of the chemical as affected by meteorological and topographical factors. However, the predicted distribution of the release chemical often fails to match the chemical distribution measured in the field because chemical transformations occurring in the atmosphere are not adequately taken into account in the various models used by DoD, Homeland Security, first responders, etc. Recognition of the importance of including kinetics of chemical reactions is critical to accurately and dependably predict the distribution of a released chemical in the atmosphere. Because atmospheric chemical reactions are fundamentally different during daytime and night time, kinetic information for both conditions must be understood and incorporated in models.

The Airbase Technologies Division of the Air Force Research Laboratory has created an atmospheric kinetic database resulting from an extensive review of the International Council of Chemical Associations (ICCA) list of High Production Volume (HPV) chemicals. Not all chemicals in the ICCA database are relevant to atmospheric dispersion; therefore, our strategy was to prioritize the chemicals based solely on the potential to pose an atmospheric threat.

After an in-depth review, we prioritized the ICCA list based on the volatility, flammability, instability, and hazard to health of the chemicals. This list is now a ranked inventory of toxic industrial chemicals (TICs). We then created a separate database containing atmospheric reaction rates for daytime and night time conditions (i.e. hydroxyl radical, nitrate radical, and ozone). Our methods for obtaining kinetic data include a review of the literature data for experimental determinations or estimates from structure reactivity relationships.

We are currently using the database to aid in development of an atmospheric chemistry software module for the dispersion model, SCIPUFF. Our atmospheric kinetic database for TICs is now available upon request.

INTRODUCTION

The atmospheric photochemical reactivity of simple volatile organic compounds (VOCs) is largely controlled by their reactions with various trace-level chemicals such as nitrate (NO_3), ozone (O_3), and hydroxyl (OH) radicals, with the OH radical playing the most important role.¹ Abstraction of a hydrogen has been shown to be the primary mechanism for these reactions. The result is formation of an alkoxy radical.² The subsequent reactions of the alkoxy radical formed determine the quantitative mix of degradation products. There is a need for understanding the fundamental effects a VOC has when it is released into the atmosphere. These effects can be considered by the following questions: (1) What is the atmospheric lifetime of the emitted VOC; (2) What are the identities and yields of the products formed during the atmospheric degradation of the VOC. The answers to these questions are ultimately grounded in the gas-phase kinetics and mechanisms of these compounds when photooxidized under atmospheric conditions. Our laboratory specializes in performing these atmospheric experiments with several publications resulting from our studies.³⁻⁹

The modelling of the atmospheric dispersion of a chemical release has reached a high level of sophistication in the description of the physical distribution of the chemical as affected by meteorological and topographical factors. However, the predicted distribution of the release chemical often fails to match the chemical distribution measured in the field because chemical transformations occurring in the atmosphere (as described above) are not adequately taken into account in the model. There is recognition within the modelling community that atmospheric chemistry algorithms need to be incorporated into today's dispersion models. This will lead to better accuracy, better response, and better preparedness to accidental or malicious releases of toxic industrial chemicals.

As an Air Force Research Laboratory, our overall mission is to protect the war fighter. Our contribution to this mission is to perform the research that is needed in atmospheric chemistry so that plumes of toxic materials are understood as to their lifetime and transformation. This allows the war fighter maximum protection and best utilization of resources. Today's enemies will use anything to try and defeat our soldiers and there is recognition within the Department of Defence that toxic industrial chemicals are becoming more of a threat. We will now present the work we have done in our effort to incorporate the atmospheric chemistry of targeted toxic industrial chemicals into DTRA's current dispersion/consequence model (Hazard Prediction and Assessment Capability, HPAC). We believe our effort enhances the capability to predict and model consequences in a contaminated environment that are a result of a terrorist attack or other major chemical release.

BODY

Selection of Priority Chemicals – General Approach

Our laboratory obtained a copy of the International Council of Chemical Associations list of 1325 chemicals. An in-depth analysis was then performed on this list to select priority chemicals based on four criteria:

- 1) Volatility
- 2) Flammability Hazard
- 3) Instability Hazard
- 4) Health Hazard

Once the priority chemicals were selected, reaction rates were researched and collected to be incorporated by the modelling community in atmospheric dispersion predictions. Research was conducted by looking at:

- 1) Literature data of experimental determinations
- 2) Estimates from structure reactivity relationships

ICCA List

The Department of Defence has become more aware of the hazards toxic industrial chemicals (TICs) pose to the troops. TICs can be released on purpose to thwart US soldiers (use of chlorine in World War I), or accidentally released with the same result (bomb dropped on a chemical plant). There are various task forces set up to look at these hazards, and one focus of these task forces is to look at High Production Volume (HPV) chemicals.

The International Council of Chemical Associations (ICCA) represents world-wide chemical manufacturers and producers and accounts for 80% of chemical manufacturing operations of HPV chemicals. In 1998 the ICCA began a global initiative to promote risk assessment as a basis for managing HPV chemicals. They recognized that various nations and regulations would approach this in different ways, so they created a list of HPV chemicals along with internationally agreed upon data on the intrinsic hazards of and initial hazard assessments of these chemicals. With this list, companies producing HPV chemicals are now responsible to apply their regulations and culture to creating hazard assessments they will adhere to.

We decided to use this list for our purposes of creating a database of TICs that are of concern due to their potential, as HPV chemicals, to become atmospheric threats to both soldiers and civilians. With this list of chemicals and their physical properties that are considered validated by an international scientific community, we began our review and found some things missing from this list. This list is not extensive and most chemical warfare agents were not included. Also missing were biological warfare agents and radio-nuclides of concern. However there is a lack of publicly accessible data on

atmospheric reactivity for these compounds, making them poor candidates for our list that is to be publicly accessible.

We then took a look at other criteria to prioritize their list. We created a Hazard Index Score (HIS) where a score of 0 – 12 was given based on flammability, toxicity, and instability.

Criteria for Prioritization

Taking the ICCA List, we created criteria for our own prioritization. We decided to only consider these High Production Volume (HPV) chemicals because non-HPV chemicals have restricted availability which leads to a decrease in probability of release. We then decided to select chemicals that had a high potential of impact on forces and civilians if released by choosing chemicals that had the ability to form a sustainable plume when released in the atmosphere. These chemicals have the following physical parameters: Boiling Point (BP) <200°C, Vapor Pressure >0.04 mm Hg. These were then further categorized as; very volatile (VV: BP -252.77°C to 40.0°C), volatile (V: BP 41.0°C to 100°C) and medium volatile (M: BP 101°C - 200°C). Then the chemicals were assessed a Hazard Index Score (HIS) based upon the National Fire Protection Agency's rating for flammability and instability and CDC's Registry of Toxic Effects of Chemical Substances' rating for health. Each of these have a score of 0 – 4; adding each score created a HIS potential of 0 – 12. Choosing the chemicals that represent a real "threat", we chose to include only chemicals that had an overall HIS 3 – 10. (No chemical achieved a HIS of 11 or 12).

The following table is the results of our re-prioritization of the ICCA List.

Table 1. ICCA Chemical List Analysis – Priority Ranking

Priority Class	Volatility Criteria	Boiling Point Range (°C)	Overall Hazard Index Score (Flammability + Instability + Health)	Number of Chemicals
1	VV	-191.49 to 37.33	7 – 10	30
2	V, M	44.04 to 156.2	7 – 10	28
3	VV	-252.77 to 45.0*	3 - 6	27*
4	V	41.5 to 99.51	3 – 6	29
5	M	100.5 – 197.3	3 - 6	79

*ammonia, anhydrous [7664-41-7] and chlorine [7782-50-5] were added to list

Results

With our chemicals chosen and prioritized, we began the work of finding all the pertinent atmospheric reactivity data that would be needed by the modelling community. We focused on the reactivity rates of daytime (hydroxyl radical, OH), night time (nitrate radical, NO₃), and ozone reactions. We performed this work by extensively reviewing the literature for well-documented and well-performed reaction rate data. After the literature was exhausted, we turned to estimation methods that are accepted by the atmospheric community. Researchers have created these methods to determine the approximate rate of a reaction based on structure reactivity.¹⁰ This is based on the observation that certain function groups of a compound tend to react at the same rate on all compounds. Disagreements between experimental and calculated rates exist, particularly with halogen-containing compounds (haloalkanes, haloalkenes, and halogenated ethers) and ethers (polyethers and cycloethers). Acceptance of structure-activity relationships (SAR) is that the rate is reliable up to a factor of 2. The data that cannot be found by either of these two methods will need the scientific community to perform experiments so as to determine their rates.

The following is an example of our results which is our Priority 1 List. We consider this list to be the most important chemicals to be researched and incorporated into the atmospheric modelling community.

Table 2. Priority 1 Compounds and their Atmospheric Reactivity Data

Name	CAS #	Reaction with OH Radicals		Reaction with Ozone		Reaction with NO ₃ Radicals	
		Reaction Rate, cm ³ mol ⁻¹ s ⁻¹	Ref	Reaction Rate, cm ³ mol ⁻¹ s ⁻¹	Ref	Reaction Rate, cm ³ mol ⁻¹ s ⁻¹	Ref
1,1-dichloroethylene	75-35-4	8.1 x 10 ⁻¹²	14	3.7 x 10 ⁻²¹	12	1.23 x 10 ⁻¹⁵	13
1,1-difluoroethylene	75-38-7	4.0 x 10 ⁻¹²	22	1.4 x 10 ⁻¹⁹	12		
2-methylpropene	115-11-7	5.14 x 10 ⁻¹¹	11	1.13 x 10 ⁻¹⁷	20	3.32 x 10 ⁻¹³	13
acetaldehyde	75-07-0	1.5 x 10 ⁻¹¹	16	<6 x 10 ⁻²¹	12	2.7 x 10 ⁻¹⁵	16
acetylene	74-86-2	7.80 x 10 ⁻¹³	16	1 x 10 ⁻²⁰	16	<1 x 10 ⁻¹⁶	16
carbon monoxide	630-08-0	2.08 x 10 ⁻¹³	16			<4 x 10 ⁻¹⁹	14
chloroethylene	75-01-4	2.36 x 10 ⁻¹²				2.93 x 10 ⁻¹⁶	14
chloromethane	74-87-3	4.2 x 10 ⁻¹⁴	16				
diethyl ether	60-29-7	1.3 x 10 ⁻¹¹	11				
dimethyl ether	115-10-6	2.8 x 10 ⁻¹²	16			<3 x 10 ⁻¹⁵	14
dimethyl sulphide	75-18-3	4.80 x 10 ⁻¹²	16	<1.0 x 10 ⁻¹⁸	16	1.1 x 10 ⁻¹²	16
dimethylamine	124-40-3	6.54 x 10 ⁻¹¹	11	2.61 x 10 ⁻¹⁸	12		
ethanethiol	75-08-1	4.64 x 10 ⁻¹¹	11			9.87 x 10 ⁻¹³	21
ethyl vinyl ether	109-92-2	4.04 x 10 ⁻¹¹	23	1.54 x 10 ⁻¹⁶	18		
ethylamine	75-04-7	2.77 x 10 ⁻¹¹	11	2.76 x 10 ⁻²⁰	12		
ethylene oxide	75-21-8	8 x 10 ⁻¹⁴	11				
hydrogen cyanide	74-90-8	3.0 x 10 ⁻¹⁴	16				
hydrogen sulphide	7783-06-4	4.7 x 10 ⁻¹²	16			<1 x 10 ⁻¹⁵	16
isoprene	78-79-5	1.0 x 10 ⁻¹⁰	16	1.27 x 10 ⁻¹⁷	16	7.0 x 10 ⁻¹³	16

isopropylamine	75-31-0	3.94 x 10 ⁻¹¹	23				
methanethiol	74-93-1	3.3 x 10 ⁻¹¹	16	4.9 x 10 ⁻¹²	16	9.2 x 10 ⁻¹³	16
methyl formate	107-31-3	2.27 x 10 ⁻¹³	19				
methyl vinyl ether	107-25-5	3.3 x 10 ⁻¹¹	11				
methylamine	74-89-5	2.2 x 10 ⁻¹¹	11	2.13 x 10 ⁻²⁰	12		
propene, pure	115-07-1	3.0 x 10 ⁻¹¹	16	1.0 x 10 ⁻¹⁷	16	9.5 x 10 ⁻¹⁵	16
propylene oxide	75-56-9	1.2 x 10 ⁻¹²	11				
tetrafluoroethylene	116-14-3	1.13 x 10 ⁻¹¹	15	4.8 x 10 ⁻²¹	15	<3 x 10 ⁻¹⁵	15
trichlorosilane	10025-78-2						
trifluorochloroethylene	79-38-9	1.3 x 10 ⁻¹⁴	17				
trimethylamine	75-50-3	6.09 x 10 ⁻¹¹	11	9.73 x 10 ⁻¹⁸	12		

The blank cells within this table indicate that there is no known literature reference and no known estimation of rate.

Conclusion

The goal of this project is to provide the kinetic data and software required for the HPAC model to incorporate the atmospheric transformation of target chemicals into its consequence prediction capabilities. Results of the model enhancements will enable HPAC to more accurately determine the distribution of a chemical's airborne plume following its release in a given environment. Our priority lists provide the kinetic data portion of this project and provide prioritization to a long list of chemicals. Work needs to be done in the future to determine the missing reactivity data – experimentally and/or improving Structure Reactivity theory. Future work would also include identifying the transformation products of these reactions, when possible, allowing the HPAC model to predict the ultimate fate of the target compound.

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